

Re-entrant Radio-Frequency Resonator Hygrometer for Fuel Cell Research and Development

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Introduction

Humidity measurement and control are crucial for efficient operation of proton-exchange-membrane fuel cells (PEMFC). In PEMFC systems, the gas diffusion layers (GDL) are responsible for ensuring optimal water vapor and liquid water transport. Excessive water in the GDL will block the flow of reactant gas to the catalyst sites. On the other hand, insufficient water reduces the ionic conductivity of proton exchange membranes degrading their performance. Recently, Mawardi *et al.* [1] used a numerical model to determine the optimum operating parameters for an automotive PEMFC system. For their specific PEMFC model, the optimum relative humidity, temperature, and pressure at the cathode are 10 %, 100 °C, and 1.5 MPa, respectively. At the anode, the optimum conditions are 100 %, 100 °C, and 0.8 MPa. Other PEMFC systems will require accurate humidity measurements at temperatures up to 200 °C in both moist air and moist hydrogen.

In this work, standardized mixtures of {CO₂-free air + water vapor} were generated at ambient pressure and then flowed through a reentrant, radio-frequency (RF), cavity resonator operating at frequencies near 370 MHz (see Fig. 1). As the generator increased the mole fraction of water vapor x_w in the mixture, the dielectric constant (relative electric permittivity) ϵ_r of the gas in the cavity increased and the resonance frequency decreased. For example, the resonance frequency decreased 0.2 % as the relative humidity increased from 0 % to 100 % at 90 °C. The repeatability of the frequency measurements was, fractionally, 4×10^{-7} , or better. This repeatability corresponds to humidity changes of 0.04 % at 90 °C. Because the resonator is robust, mechanically simple, moderately-sized (7 cm outside diameter, 7 cm high), and constructed from corrosion-resistant materials (Inconel [2] with gold and ceramic seals), it is a promising candidate to become a reference standard for humidity measurements up to the highest temperatures and pressures proposed for fuel cell operation. Similar resonators have been used at the National Institute of Standards and Technology (NIST) to accurately measure the dielectric constant of gases and of liquid water and also to determine the dipole moments of gases. [3,4,5].

Theory of Measurement

For design purposes, we consider CO₂-free air and water vapor to be a mixture of non-interacting species. For such a mixture, an approximate expression [6] for the dielectric constant is:

$$\frac{\epsilon' - 1}{\epsilon' + 2} \approx \sum_i \rho_i A_i + \rho_w \left(A_w + \frac{B_w}{T} \right) \quad (1)$$

In Eq. (1), ϵ' is the real part of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$; ρ_i and A_i are the molar density and the molar polarizability of the i th species in air ($i = \text{N}_2, \text{O}_2, \text{Ar}$); ρ_w is the molar density of water vapor, and T is the absolute temperature. Reference [7] tabulates values of the Debye constants [A_w and B_w in Eq. (1)] from seven sources. These sources predict values of $(A_w + B_w/T)$ ranging from 60.31 to 61.39 cm³·mol⁻¹ at 90 °C. In Eq. (1), we used the mean value, 60.91 cm³·mol⁻¹. For air, the A_i are nearly independent of the temperature and have a very small density dependence. At 90 °C and 100 kPa, $A_{\text{N}_2} = 4.3882$ cm³·mol⁻¹ and $A_{\text{air}} = 4.1561$ cm³·mol⁻¹, where “air” is CO₂-free and dry. [8] In contrast, the values of $(A_w + B_w/T)$ are density dependent.

In Eq. (1), we substitute products of (mole fractions) \times (partial pressures) for the densities and we account for real gas effects with the second virial coefficient for the mixture $B_{\text{mix}}(T)$ to obtain:

$$\frac{\varepsilon' - 1}{\varepsilon' + 2} = \frac{P}{RT(1 + B_{\text{mix}}P/(RT))} \left[\sum_i x_i A_i + x_w (A_w + B_w/T) \right] \quad (2)$$

Here, R is the universal gas constant and P is the total pressure. We used Eq. (2) to determine values of $x_w(\text{resonator})$ from the measurements of ε' , P and T ; we obtained B_{mix} , $(A_w + B_w/T)$, and A_i from the literature. In Table 1, the values of $x_w(\text{resonator})$ are compared with the values $x_w(\text{generator})$ deduced from the dew-point temperature in the humidity generator, the saturated vapor pressure of water, and the enhancement factor $f_{\text{mix}}(P, T)$.

The Measurement of Dielectric Constant

In this study, we used one of the two resonators described in detail by Goodwin *et al.* [3] Using a network analyzer, we measured the transmission S_{21} through the resonator as a function of the frequency f near 370 MHz. We deduced the complex resonance frequency $F = f_\alpha + ig_\alpha$ by fitting the values of S_{21} to the resonance function:

$$S_{12}(f) = \frac{Af}{f^2 - F^2} + B + C(f - f^*) + D(f - f^*)^2 \quad (3)$$

Here f^* is any fixed frequency near f_α and the fitting parameters A , B , C , and D are complex numbers. Thus, eight parameters were used in the fit. In dry gas, repeated determinations of f_α had a fractional standard deviation $\sigma < 10^{-7}$; for the moist gases, $\sigma < 4 \times 10^{-7}$.

Hamelin *et al.* [4] give a complete equation relating the complex resonance frequency $F = f_\alpha + ig_\alpha$ to the dielectric constant of the gas-filled resonator. (We call f_α the “resonance frequency” and g_α

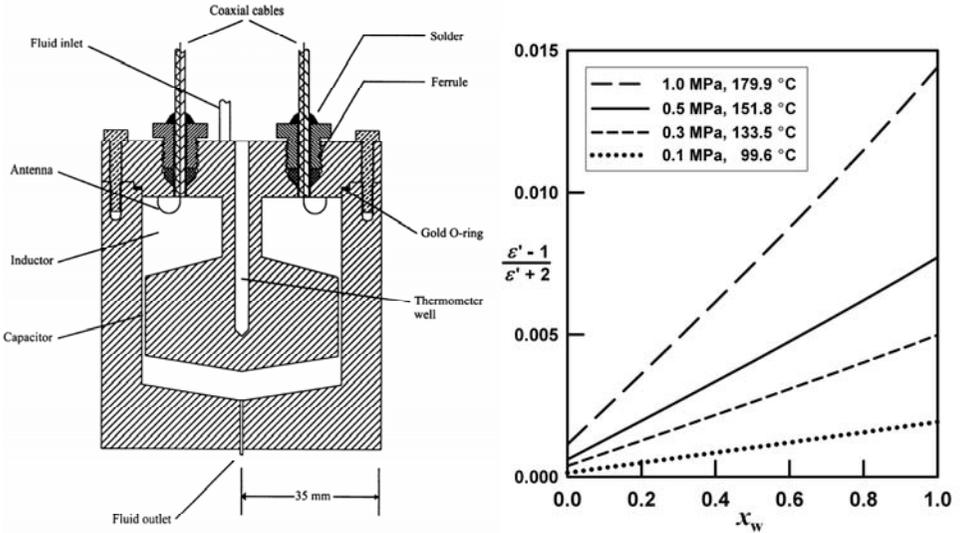


Figure 1. Left: Cross section of re-entrant resonator. Right: Mole fraction of water vapor as a function of $(\varepsilon' - 1)/(\varepsilon' + 2)$ calculated from Eq. (2) for total pressures from 0.1 MPa to 1.5 MPa.

the “resonance half-width”). Corrections must be applied for the electrical resistivity of the resonator’s wall and for the coupling of external circuitry to the resonator. We determined these corrections from measurements of the resonance frequency when the resonator was filled with dry nitrogen and from the frequency dependence of the half-width as the water concentration was varied. If $F_0 = f_0 + ig_0$ is the complex resonance frequency of the evacuated resonator, and g_{0s} and g_{as} are the components of g_0 and g_a due solely to the resistive losses, the dielectric constant may be obtained from:

$$\epsilon' = \left(\frac{f_0 + g_{0s}}{f_a + g_{as}} \right)^2 . \quad (4)$$

For precise work, Eq. (4) must be corrected for the resonator’s deformation with pressure. [4]

Preliminary Results

To test the performance of the resonator-hygrometer, we connected the resonator to the output of the NIST Hybrid Humidity Generator and measured the dielectric constant for water vapor-air mixtures of varying water concentration. The generator produced a gas stream of CO₂-free atmospheric air saturated with water vapor at carefully-defined dew-point temperatures, all of which were below the temperature of the thermostatted bath containing the resonator. The design of the saturation section of the Hybrid Humidity Generator follows the general principles of past NIST humidity generators [9]. Air containing mole fractions of water vapor from 0.081 to 0.567 was introduced into the inlet of the resonator at a flow rate of 360 cm³·min⁻¹. When the temperature, pressure and flow of the sample air reached stable conditions, resonance frequency and half-width were measured. The dielectric constant was calculated using Eq. (4) and reference values [f_a and g_{as} in Eq. (4)] that had been measured while dry nitrogen flowed through the resonator. (Row 1 of Table 1.)

The mole fraction of water $x_w(\text{resonator})$ was calculated from Eq. (2) using literature values of $B_{\text{mix}}(T)$, the polarizability of nitrogen, water, and CO₂-free air. The last column of Table 1 is the difference $\Delta x_w \equiv x_w(\text{resonator}) - x_w(\text{generator})$. We deduced $x_w(\text{generator})$ from the dew-point temperature in the humidity generator, the saturated vapor pressure of water, and the values of the enhancement factor. [10,11] Remarkably, $|\Delta x_w| \leq 0.0026$. At the higher values of x_w , the uncertainties of Δx_w and $x_w(\text{resonator})$ are dominated by the uncertainty of $(A_w + B_w/T)$.

Table 1. Properties of the generated gas stream (total pressure P , water vapor mole fraction x_w , dew-point temperature t_{dp}); properties measured with the resonator (temperature t , frequency, half-width); dielectric constant computed from f and g , and the inconsistency of x_w . Row 1 is for N₂.

generated gas stream			measured from resonator				comparison
P (Pa)	x_w generator	t_{dp} (°C)	t (°C)	f (MHz)	g (MHz)	ϵ'	$x_w(\text{resonator}) - x_w(\text{generator})$
100626	0.0000	n.a.	90.193	367.76836	0.79917	1.0004372	-0.0002
100656	0.0812	41.78	90.195	367.68643	0.79908	1.0008826	0.0011
100597	0.1992	59.93	90.180	367.56450	0.79898	1.0015465	0.0000
100471	0.4614	79.26	90.192	367.29138	0.79872	1.0030349	-0.0012
100393	0.5670	84.41	90.203	367.18174	0.79861	1.0036317	-0.0026

The excellent agreement of the resonator-hygrometer with the generator over a broad range of water vapor concentrations demonstrates that the hygrometer can serve as a reliable reference standard, at water vapor concentrations well in excess of the upper limits of the NIST Hybrid

Humidity Generators. With its robust design, inherent stability, and well-understood theory of operation, we expect that the RF-resonator hygrometer will enable traceable measurements of water vapor mole fraction over the full range of temperatures and pressures necessary for fuel cell applications.

Acknowledgments

We thank Wyatt Miller and Christopher Meyer for their valuable and timely contributions to the NIST Hybrid Humidity Generator. We thank Allan Harvey for suggesting improvements to our draft manuscript.

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